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Monte Carlo simulations on concentration self-quenching by statistical traps

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We present high accuracy Monte Carlo simulations on the steady state fluorescence quantum yield and anisotropy for systems in which concentration self-quenching due to incoherent energy transfer between randomly distributed molecules occurs. A simple model of self-quenching is considered, in which luminescent molecules within a critical distance of each other act as perfect traps. The simulations are based on the complete solution of the coupled rate equations for a randomly chosen distribution of molecules in a finite box. Finite size effects are systematically investigated. The results are used to assess the validity of simple analytic theories, such as Burshtein's theory of hopping transfer, which is found to give a good semiquantitative description of the fluorescence quantities. Furthermore, we show that truncating the transfer rate in such a way that, on the average, 10–20 molecules are within reach of an excitation residing on a given molecule, induces large deviations in the yield. We point out that this is a serious source of error in previous simulations.

I. INTRODUCTION

Incoherent energy transfer in disordered systems has provided an interesting field of research for many years.[1] Fluorescence measurements have revealed a wide variety of both organic and inorganic systems in which this mechanism of excitation transport plays an important role, the chlorophyll photosynthetic system and rare earths compounds, respectively, being two of the best known examples. From a theoretical point of view, the disorder poses great problems in obtaining analytic results for the various quantities of interest, such as the diffusion coefficient, the time-dependent intensity, the quantum yield, and the anisotropy of emission. Systematic theories[2–9] have yielded new insights in these problems, as well as some practical results, but have not yet led to, e.g., a satisfactory description of the high density and (or) long time regime of excitation migration. Heuristic models[10–12] have been very useful in many ways, but cannot be corroborated by rigorous theories, where the latter have not yet been successful. For such reasons computer simulations continue to be of invaluable help in gaining further insight in transfer phenomena.

This work is concerned with extensive, high accuracy Monte Carlo simulations in a simple model for self-quenching in two and three dimensions. This phenomenon occurs in several systems consisting of a single type of molecules when pairs of them start to act as traps for excitations at sufficiently high densities.[11(b),13–15] A sophisticated theoretical treatment of self-quenching is difficult both for the high densities at which it takes place, and because of the donor–trap nature of the system. The latter problem is further compounded by the fact that the traps are of a statistical nature: Their distribution is not independent of that for the donors, because two donors combine to a trap when sufficiently close; mainly because of the high densities involved, also the simulations reported here are intricate, although the method used is very direct. The fact that an early attempt[14(a)] at simulating this very model has been made, with which we find our results to be at variance, attests to this difficulty. We have found that a serious source of the discrepancies lies in the neglect of possible random walks caused by a truncation of the transfer rate beyond a given (too small) distance, as used in Ref. 14(a). We expect that the significance of this observation will not be confined to the present model.

With the results of this simulation, one can judge the performance of intuitive models for self-quenching. In previous work[16] we have argued the merits of a heuristic hopping model,[11] which includes both a simple description of the donor and trap distributions and an intuitive but powerful correction for backtransfer,[10] by comparison with some exact results of hopping theory. Of course, even exact hopping theory yields only an approximate description of the microscopic transfer kinetics. In this work we establish, however, that the hopping theory of energy transfer captures rather well the main features of both the quantum yield and the emission anisotropy found in our simulations. This then also means that in practice the heuristic hopping model gives a reliable semiquantitative description of self-quenching.

The outline of this paper is as follows: In Sec. II we first briefly describe the system studied, and then confine ourselves to an explanation of the method of simulation. We calculate the steady state quantum yield and emission anisotropy; for a precise definition of those quantities, and for their analytic expressions in heuristic hopping models, we refer to our previous paper.[16] In Sec. III we discuss specifics of the simulation at some length. We feel that this is necessary to show the complexity of such simulations, and to give the reader explicit information by which the quality of our results can be judged. In Sec. IV the results are presented, and comparison with (hopping) theory is made. Section V contains a summary of our conclusions and some final observations.

II. METHOD OF SIMULATION

Let us first, for completeness, give a brief description of the system studied (for more details we refer to Ref. 16). Luminescent molecules at number density ρ are randomly

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distributed in a Δ-dimensional medium. Between them incoherent transfer of excitation energy occurs with a multipolar transfer rate $w(r) = \tau_0^{-1}(R_0/r)^m$, where τ_0 is the radiative lifetime of the excited state of interest. In this system self-quenching is modeled, by considering two molecules within a distance R_s (statistical trap radius) of one another as non-fluorescent traps. The total intrinsic lifetime τ, together with τ_0, determines the quantum yield $Q_0 = \tau/\tau_0$ at very low density. It is useful for future reference to introduce the reduced density $\hat{\rho} = V_\Delta R_0^\Delta \rho$ (V_Δ is the volume of a Δ-dimensional unit sphere) and the dimensionless trap radius $r_s = R_s/R_0$.

We now turn to the Monte Carlo simulations, which, like those performed by Ching *et al.*[17] in the time domain for pure donor systems, are entirely based on the coupled rate equations (CRE) that govern the occupation probabilities $p_i(t)$ of the individual donors ($i = 1,...,D$). These are given by

$$\frac{dp_i}{dt} = -\sum_j \mathbb{W}_{ij} p_j(t)$$

with

$$\mathbb{W}_{ij} = \delta_{ij} w_i - w_{ji}. \tag{2.1}$$

$\mathbb{W}$ is the relaxation matrix, in which w_i is the total transfer rate from donor i to all other donors and traps, and w_{ji} is the rate from donor j to donor i. Suitable summations, which amount to configurational averages, of the formal solutions

$$p_i^k(t) = [\exp(-\mathbb{W}t)]_{ik}, \tag{2.2}$$

for the occupation probabilities with initial condition $p_i^k(0) = \delta_{ik}$, yield two interesting time-dependent characteristics of the transfer process following δ pulse excitation at $t = 0$. These are the total donor intensity $N(t)$ and the conditional probability $N_0(t)$ that an initially excited donor is also excited at time t. The Laplace transforms of these two quantities,

$$\tilde{N}_0(\tau^{-1}) = \frac{\tau}{D}\sum_i [(\mathbb{I} + \tau\mathbb{W})^{-1}]_{ii} \tag{2.3}$$

and

$$\tilde{N}(\tau^{-1}) = \frac{\tau}{D}\sum_{ij} [(\mathbb{I} + \tau\mathbb{W})^{-1}]_{ij} \tag{2.4}$$

($\mathbb{I}$ denotes the identity), determine the steady state donor quantum yield and the emission anisotropy (see Ref. 16). One sees that the problem amounts to calculating the inverse of the matrix $\mathbb{I} + \tau\mathbb{W}$, and determining its trace and the sum of all its elements. Evidently, this cannot be done analytically, but Eqs. (2.3) and (2.4) can be exploited very well in simulations.

In our simulations, M particles are positioned randomly in a square or cubic box. The length of the box edge is related to the density at which one wants to carry out the simulation. In terms of the distance x_{ij} between molecules i and j, measured in units of the box length, the dimensionless transfer rate is

$$\tau w_{ij} = Q_0 \left[\frac{\hat{\rho}}{V_\Delta M}\right]^{m/\Delta} x_{ij}^{-m}. \tag{2.5}$$

Traps are detected by calculating all intermolecular distances and comparing them to the statistical trap radius in units of the box length

$$x_s = r_s \left[\frac{\hat{\rho}}{V_\Delta M}\right]^{1/\Delta}. \tag{2.6}$$

Note, that Eqs. (2.5) and (2.6) reflect the scaling dependence on the system parameters Q_0, ρ, R_s, and R_0 discussed in Ref. 16.

The finite size of the configurations generated of course introduces errors. Molecules near the boundary will have few neighbors, so that they pass on their excitation too slowly, and excitations reaching the wall will be reflected, so that they immediately reenter a region that they were just leaving. In order to reduce these effects, we impose periodic boundary conditions, together with a minimum image convention. This means that the surroundings of each molecule are assumed to exist of a box (with the size of the basic box) centered around it, in which either the original or the nearest periodic image of every other molecule lies.

For the system defined in this manner the number D of donors is obtained, and simultaneously the $D \times D$ matrix $\mathbb{I} + \tau\mathbb{W}$ is filled. Note, that this matrix is symmetric and positive definite, which ensures the existence of the inverse and facilitates its numerical evaluation. In the thermodynamic limit, Eqs. (2.3) and (2.4) automatically generate complete configurational averages, but, since individual simulation runs cannot be performed for too large M (because of CPU time consumption as well as stability limitations), one has to carry out a suitable average over a number of systems $s = 1,2,...,S$, through

$$\tilde{N}_0(\tau^{-1}) = \frac{\tau}{\Sigma_s D_s}\sum_s \sum_i [(\mathbb{I} + \tau\mathbb{W}_s)^{-1}]_{ii} \tag{2.7}$$

and

$$\tilde{N}(\tau^{-1}) = \frac{\tau}{\Sigma_s D_s}\sum_s \sum_{ij} [(\mathbb{I} + \tau\mathbb{W}_s)^{-1}]_{ij}, \tag{2.8}$$

where $\mathbb{W}_s$ is the relaxation matrix of the sth simulated system, and D_s the number of donors in it. The reason for averaging in this manner is best understood by imagining one giant system, built up out of the individually generated systems and without any intersystem interactions.[18]

III. SPECIFICS OF THE COMPUTATION

Simulations along the lines described in the previous section are performed for a three-dimensional system with $r_s = 0.20$, $Q_0 = 1/3$, and $m = 6$. These specific parameters are chosen, because they cover previous simulations (by a different method) of Porter and Beddard (PB)[14(a)] on *in vitro* chlorophyll. Data are obtained for densities varying from $\hat{\rho} = 0.05$ up to $\hat{\rho} = 100$. The number of molecules in one configuration, and the number of configurations at one density, needed in order to generate reliable data, depends on the concentration. At low densities ($\hat{\rho} < 1$), 500 runs of 100 molecules each are sampled, at higher densities 1000 runs of 150 molecules are needed. The matrices are inverted by standard routines. The numerical procedures are tested by checking the created donor density against the analytically expected value of $\rho_d = \rho \exp(-\hat{\rho} v_s)$,[16] and by checking whether a system in which no traps are present indeed gives a yield equal to unity. The latter test turns out to be particular-

ly useful to detect stability problems of the matrix inversion. Observed deviations all appear to lie well within allowed boundaries.

Furthermore, elaborate tests are carried out on the convergence with respect to system size, by calculating at different values of M (100,150,200,250) for several densities. The most serious problems with the convergence are encountered in the intermediate density regime ($5 \lesssim \hat{\rho} \lesssim 20$). This can easily be understood. At low densities, almost no hops are made during the lifetime τ, since the intermolecular transfer rates simply are too small. As a consequence, an excitation will not be able to walk distances of the order of the box length, so that it does not notice the finite size. At very high densities, the excitation would have been able to travel distances many times the box length, if not a macroscopic fraction of the molecules to which it hops had been traps. On these traps the walk ends, so that a typical walk lasts only a few steps, and the finite size again is not a severe limitation. At moderate densities, precisely in the region where the yield really starts to decrease, the hopping is still fast, and the number of traps is not yet high enough to prevent excitations from walking through the same system (periodic boundary conditions) several times. If in a real system the excitation is in a region, which happens to have few traps as a result of fluctuations, it has an enhanced probability to reach the boundary of this area and enter another one with probably more traps. In the simulated system, however, the excitation enters the same box time and again. It is thus clear that the periodic boundary conditions artificially increase the quantum yield $[\tau^{-1}\tilde{N}(\tau^{-1})]$, and this is precisely what is observed when one analyzes the data for different system sizes. The effect of the finite system size on the anisotropy is furthermore determined by effects on $\tau^{-1}\tilde{N}_0(\tau^{-1})$, which are mainly caused by excitations returning to their initial donors, after walking through the box. For a system consisting of M donors, numerical results for densities at which $\tau^{-1}\tilde{N}_0(\tau^{-1})$ gets in the order of M^{-1} (the minimum possible value) cannot be trusted. From our results, however, it appears that in the region where this happens, the fraction of traps is already so large, that it is highly improbable for an excitation to walk around the system and return to its initial donor. We estimate errors caused by such walks not to exceed 1% in all our calculations.

More quantitative insight with respect to the system size needed at given density is gained from the scaling behavior of the diffusion coefficient in donor systems. By a straightforward generalization of the arguments of Haan and Zwanzig,[5] it can be shown that in a donor system with density $\hat{\rho}_d$ the diffusion coefficient $D \sim \hat{\rho}_d^{(m-2)/\Delta}$. From this, the mean squared distance traveled by an excitation during time t is given by $L^2(t) = \gamma R_0^2 \hat{\rho}_d^{(m-2)/\Delta} t/\tau$, with γ a numerical constant, depending on m, Δ, and Q_0. The system must be large enough to ensure that L does not exceed the box length for several lifetimes τ. Thus, for $m = 6$, $\Delta = 3$, and $Q_0 = 1/3$, the minimum number of molecules required is $M_m \sim \rho_d L^3(\tau) \sim \hat{\rho}_d^3$, with a proportionality constant of order unity.[5,6] For $\hat{\rho} = 5.0$ one finds $M_m \simeq 100$, which is indeed close to the value (150) that we have to use in order for the results to converge. For $\hat{\rho} = 10.0$ one finds $M_m \simeq 800$. This would have made the calculations impossible, as 250×250 matrices are about the largest that we can still invert in a stable way within reasonable time, if not about one in ten molecules had been a trap at this density. This explains why taking a system of the order of $5 \times 5 \times 5$ molecules is still enough to prevent finite size effects from dominating. It is clear that at, for instance, $r_s = 1/7$ (other parameters unchanged), which is the second case considered by PB, the mean fraction of traps is considerably lower ($\hat{\rho}_t \simeq \hat{\rho} r_s^3$) so that finite size effects will be more important there. Indeed, we do not observe a convergence in this case, e.g., at $\hat{\rho} = 20.0$ a decrease in yield of up to 10% still occurs between $M = 150$ and $M = 200$. In two dimensions, $M_m \sim \rho_d L^2(\tau)$, which is again proportional to $\hat{\rho}^3$ but now the fraction of traps is roughly $\hat{\rho} r_s^2$. This is a factor of r_s^{-1} larger than in three dimensions at the same density. So one expects, and we indeed encounter, less finite size effects in two dimensions.

IV. RESULTS OF THE SIMULATIONS

The results for the yield and anisotropy in three dimensions for $r_s = 0.20$, $Q_0 = 1/3$, and $m = 6$ are shown in Fig. 1. Errors are far smaller than the size of the dots that mark the

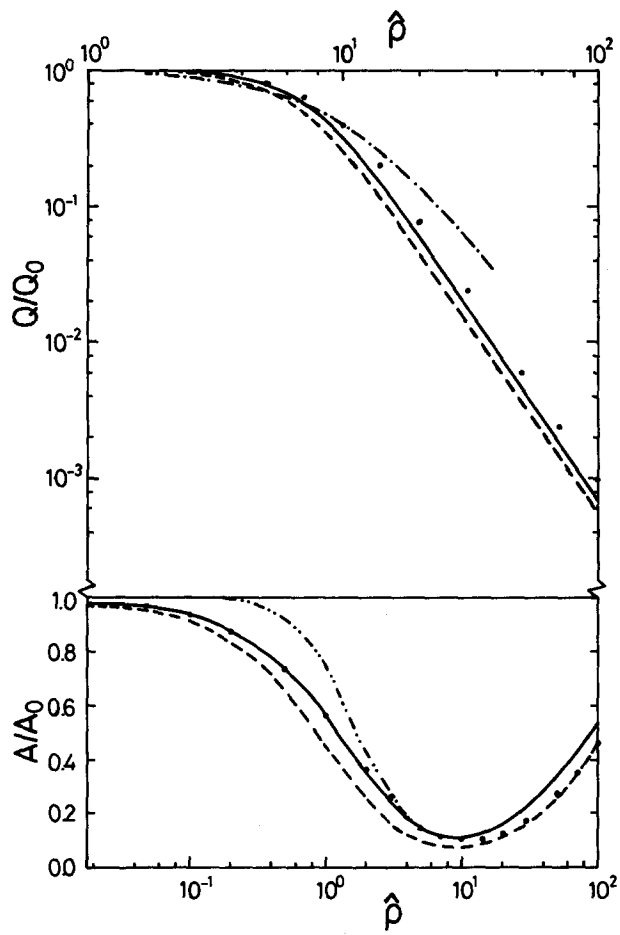

FIG. 1. Yield and anisotropy in a three-dimensional system with $r_s = 0.20$, $Q_0 = 1/3$, and $m = 6$. Data from the nbt-hopping model (- - -), cosh-hopping model (—), Monte Carlo simulations performed in this study (●), Monte Carlo simulations from Ref. 14(a) (-·-·-), and for the model defined by Eqs. (4.1) and (4.2) (-···-···-). Note the different density scales for top and bottom figures.

data points. They are estimated by comparing results for ten blocks of configuration runs, as well as by comparing the variation of results with M. Also given in this figure are the old data of PB for the quantum yield (they have not calculated the anisotropy). Although PB do not give any information on errors in their simulation, one may safely conclude that their data are at variance with ours. Taking account of initial trap absorption, by simply multiplying the yield by the fraction of molecules that are donors, as PB probably have done, would only make the discrepancy larger. We cannot explain deviations in the low density regime; however, we are convinced that, at high densities, their results are incorrect because of the "long distance" cutoff imposed on the transfer rate. At first sight it seems quite reasonable to create a density dependent cutoff for the transfer rate. This can be done by setting the transfer rate equal to zero beyond a distance R_c determined by $\rho V_\Delta (R_c^\Delta - R_s^\Delta) = M_c$, where M_c is a fixed number of molecules. From a numerical point of view, this may be very attractive, especially in a simulation such as that of PB, who really *sample* random walks, whereas we formally sum over all random walks, which results in the matrix inversion. Thus by creating a cutoff, only a few molecules (M_c on the average) have to be considered as next possible hosts for the excitation. This saves a lot of computing time, and may be the practical reason why PB's simulation was feasible at all ten years ago. In order to investigate the validity of such a cutoff, which PB performed at $M_c \simeq 11$, we carried out additional Monte Carlo simulations with cutoffs at $M_c = 10$ and $M_c = 20$, for three densities. The results for the yield are presented in Table I. Note that errors of up to 50% are generated in the case $M_c = 10$, which explains an important part of the deviations of PB's data in Fig. 1. The influence of the cutoff on the anisotropy is hardly significant, which can be understood from the fact that this quantity is the ratio of $\tilde{N}_0$ and $\tilde{N}$, which are both affected by a cutoff in the same sense.

In order to obtain an independent, more analytic check on the order of magnitude of this effect, we have calculated the average waiting time for excitations on donors as a function of the density and at different values of M_c. It can easily be shown that this quantity equals $\tilde{F}(\tau^{-1})$, the Laplace transform of $F(t)$, which is defined by Eq. (2.9) in Ref. 16. Taking into account a cutoff at R_c, one obtains an expression for the waiting time that closely resembles Eq. (3.10) of Ref. 16, except that two extra terms are present in the exponent, analogous to those representing the R_s cutoff. $\tilde{F}$ is obtained by numerical integration. Relative deviations of waiting times for $M_c = 10$ and 20, compared to the case $M_c = \infty$, are given in Fig. 2. As is seen, for $M_c = 10$, induced errors amount to 10%–40% in the density interval where the decay occurs. Evidently, when the waiting times are so heavily influenced by the cutoff, the same will also be true for the whole transfer kinetics.

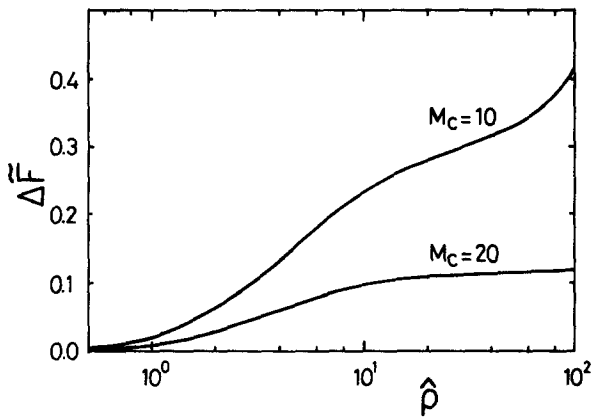

FIG. 2. Relative error in the average waiting time caused by a cutoff in the transfer rate corresponding to $M_c = 10$ and $M_c = 20$, as a function of the reduced density, in three dimensions. Parameters as in Fig. 1.

Next we compare the heuristic hopping model results for the yield and anisotropy,[16] with our "exact" Monte Carlo results. Curves for the no-back-transfer (nbt) and cosh-hopping models are shown in Fig. 1. We make the following observations: (i) Both the nbt and the cosh curves for the yield closely resemble the "exact" MC curve in shape. The most striking manifestation of this resemblance is the *almost linear* part of the decay (in the log Q/Q_0–log $\hat{\rho}$ plots) where the three curves are practically parallel. This part corresponds to one of two interesting limiting regimes for the scaling parameters, namely $\hat{\rho} Q_0^{\Delta/m} \gg 1$ and simultaneously $\hat{\rho} v_s \ll 1$ ($v_s = r_s^\Delta$). Although strictly speaking these limits are contradictory (unless Q_0 or r_s have limiting values), a lowest order expansion in $1/(\hat{\rho} Q_0^{\Delta/m})$ and $\hat{\rho} v_s$ turns out to be useful, owing to the smallness of v_s. Results are shown in Table II. The calculated slope of the log Q/Q_0–log $\hat{\rho}$ plot is seen to have the value of $-(1 + m/\Delta)$ both for the nbt and the cosh model, and, for $m = 6$ and $\Delta = 3$, this is very close to

TABLE I. Comparison of the yield for different long distance cutoffs in the transfer rate. Simulations in three dimensions at $r_s = 0.20$, $Q_0 = 1/3$, and $m = 6$. In brackets the absolute errors are given.

	Q/Q_0		
$\hat{\rho}$	No cutoff	$M_c = 20$	$M_c = 10$
14.0	0.195	0.221	0.259
	(0.002)	(0.002)	(0.003)
30.0	0.248×10^{-1}	0.293×10^{-1}	0.358×10^{-1}
	(0.002×10^{-1})	(0.003×10^{-1})	(0.005×10^{-1})
70.0	0.241×10^{-2}	0.284×10^{-2}	0.350×10^{-2}
	(0.002×10^{-2})	(0.002×10^{-2})	(0.002×10^{-2})

TABLE II. Lowest order behavior of the yield in the regimes $\hat{\rho} Q_0^{\Delta/m} \gg 1$, $\hat{\rho} v_s \ll 1$, and $\hat{\rho} Q_0^{\Delta/m} \gg 1$, $\hat{\rho} v_s \gg 1$, respectively, for the analytic models mentioned in the text. g stands for $\Gamma(1 + m/\Delta)/[\Gamma(1 - \Delta/m)]^{m/\Delta}$, with $\Gamma(x)$ the gamma function.

	Q/Q_0	
	Intermediate density	Infinite density
nbt hopping	$g 2^{1-\Delta/m} (Q_0 \hat{\rho}^{1+m/\Delta} v_s)^{-1}$	$g 2^{m/\Delta - 1} (Q_0 \hat{\rho}^{m/\Delta})^{-1}$
cosh hopping	$g 2^{m/\Delta - 1} (Q_0 \hat{\rho}^{1+m/\Delta} v_s)^{-1}$	
Equation (4.1)	$(Q_0 \hat{\rho}^{1+m/\Delta} v_s)^{-1}$	$(Q_0 \hat{\rho}^{m/\Delta})^{-1}$

that observed in the curves. The other limiting regime $\hat{\rho}v_s \gg 1$ is of less practical importance (negligible yield, probably inconsistent with densest molecular packing), but, for completeness we also give the results in this case. The interesting conclusion for experimental work is the existence of the linear regime, and the relation of the measured slope to m. (ii) The nbt curve for the yield lies 40% too low in the decay region, while the deviation is approximately 25% for the cosh curve. Thus the intuitive treatment of backtransfer leading to the cosh model, reduces these deviations almost by a factor of 2. The half-quenching concentration in both models is very close to the exact value (20% and 8% off, respectively), but, although this parameter is of practical importance in estimating R_0 from experiment, it does not give a fair indication for the correctness of a theory, since the decay is extremely steep. (iii) As the yield begins to fall off, the anisotropy goes through a minimum and then starts rising again. It is described *extremely well* by the cosh-hopping model right into the minimum. These three conclusions basically hold in two dimensions as well. In that case, the cosh model predicts yields again about 25% too low, whereas the nbt results are now 50%–60% too low. Data are presented in Fig. 3.

To judge the performance of the hopping models as compared to other simple analytic theories, we also present in the figures results obtained from a very rough model of transfer kinetics, which has been used recently in the interpretation of experimental results for the yield.[15] In this model, all excitations are assumed to hop between molecules at a rate $k_{\rm hop} = \tau_0^{-1}\hat{\rho}^{m/\Delta}$, which is the appropriate transfer rate between two molecules at average distance $(V_\Delta \rho)^{-1/\Delta}$. One may now approximate $N_0(t)$ by $\exp(-k_{\rm hop}t)$ and $N(t)$ by $\exp(-k_{\rm hop}f_t t)$, where f_t is the fraction of the molecules that are traps. Note that these quantities now decay exponentially, because the disorder has been averaged out at a very early stage. One thus finds for the steady state quantities

$$Q/Q_0 = [1 + Q_0\hat{\rho}^{m/\Delta}(1 - \exp[-\hat{\rho}v_s])]^{-1} \quad (4.1)$$

and

$$A/A_0 = 1 - \frac{Q_0\hat{\rho}^{m/\Delta}\exp[-\hat{\rho}v_s]}{1 + Q_0\hat{\rho}^{m/\Delta}}. \quad (4.2)$$

Curves predicted by these equations, are also given in Figs. 1 and 3. In three dimensions the yield (4.1) lies in between the two heuristic hopping models with a somewhat steeper slope in the linear part of the curve (lowest order limiting behavior is given in Table II); it is not drawn in Fig. 1 for reasons of clarity. Furthermore, the anisotropy is clearly much better predicted by the hopping model. In two dimensions, not only the anisotropy, but also the yield is very poorly presented by Eqs. (4.1) and (4.2). The yield is too low, compared to the Monte Carlo results, by a factor of approximately 10.

Since the cosh-hopping model gives a good semiquantitative description for the yield and the anisotropy, it is worthwhile to discuss the influence of varying the system parameters r_s, Q_0, and m within this model. We will concentrate on the yield in the three-dimensional case and, without giving graphs, we mention the following characteristics: (i) For $m = 6$ and $Q_0 = 1/3$, r_s has been varied from 0.10 to 0.50. It is obvious that the yield decreases with increasing r_s. Furthermore, the different curves are actually observed to be parallel in the decay region, with slopes close to the r_s-independent value of $-(1 + m/\Delta)$ predicted above. Only for $r_s \gtrsim 1/3$, the linear behavior gets distorted, since $\hat{\rho}v_s$ is not really a small parameter anymore, so that a slow transition to the real infinite density limit, where $Q/Q_0 \sim \hat{\rho}^{-m/\Delta}$, is observed. (ii) Curves have been obtained for $m = 6$, $r_s = 0.20$, and Q_0 varying from 0.10 to 0.90. It appears that the yield decreases with increasing Q_0. This can easily be explained: $1 - Q/Q_0$ can be interpreted as the average fraction of the excitations that walk into a trap before they decay spontaneously,[16] and increasing Q_0 is equivalent to increasing the lifetime. At high densities a very simple dependence on Q_0 exists. Recalling that $Q/Q_0 = \tau^{-1}\tilde{N}(\tau^{-1})$ and realizing that at high densities $N(t)$ decays long before the lifetime τ has elapsed, one finds $Q/Q_0 \sim \tau^{-1} \sim Q_0^{-1}$. This is confirmed by the data, which show this simple dependence already at yields of the order of 0.10 ($\hat{\rho} \simeq 20$). In view of the scaling behavior deduced in Ref. 16, this implies that an important part of the decay is described by

$$Q/Q_0 = [\hat{\rho}^{m/\Delta}Q_0]^{-1}q(\hat{\rho}v_s) \quad (\hat{\rho}\ \text{large}). \quad (4.3)$$

Here q is a single-parameter scaling function, with a form depending on Δ and m, which, for the analytic models mentioned above and in the different limiting regimes, can be

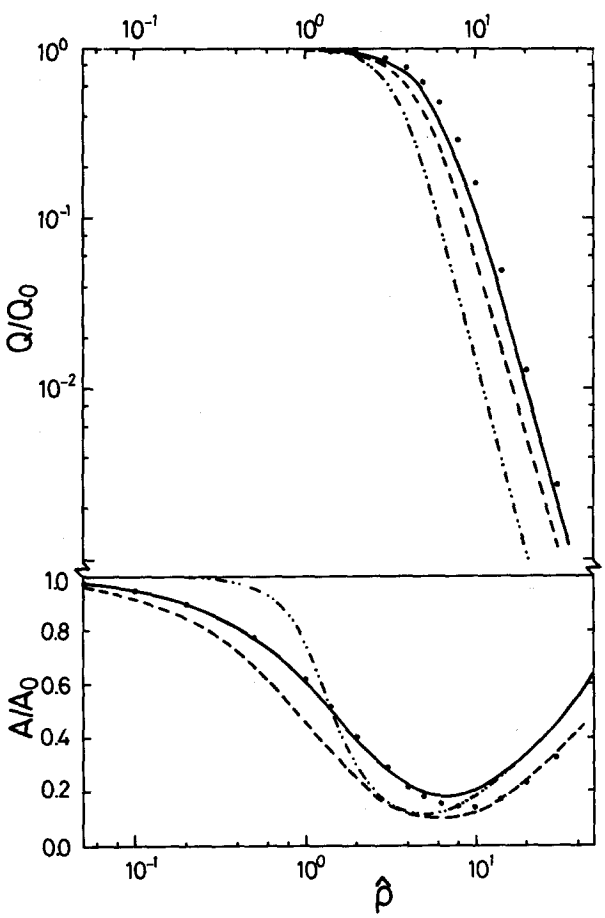

FIG. 3. Yield and anisotropy in a two-dimensional system with $r_s = 1/7$, $Q_0 = 1/3$, and $m = 6$. Curves coded as in Fig. 1.

easily read off from Table II. It would be interesting to check the scaling (4.3) and to derive an exact form for q, by means of Monte Carlo calculations. This, however, would require many more simulations than we have carried out thus far. (iii) With respect to m variations, we only mention here that the linear part of the decay gets steeper with increasing m in accordance with the predicted slope $-(1+m/\Delta)$.

V. CONCLUDING REMARKS

In this study, high accuracy Monte Carlo simulations on self-quenching systems have been presented. These have been carried out by generating random configurations of luminescent molecules, followed by calculation and inversion of the system's relaxation matrix. By this method, all possible random walks are taken into account. One of the most striking outcomes of these calculations is the sensitive dependence of the quantum yield on a "long distance" cutoff of the transfer rate performed in the way described in Sec. IV. We have pointed out that this is a serious source of error in the simulations of Porter and Beddard. This also means that since the slope of the decay (in $\log Q/Q_0 - \log \rho$ plots) does not vary with R_0 and hardly with R_s, the experimental data on *in vitro* chlorophyll interpreted by PB cannot be described by the simple model of self-quenching that they propose. In view of our results, these data will have to be reexamined in the context of a more complicated model. A general consequence of the sensitivity mentioned is the impossibility to characterize the relaxation matrix at high concentrations as a sparse matrix, which precludes the use of more sophisticated inversion techniques for very large systems ($M > 1000$), as should be studied to avoid finite size effects at low values for r_s.

Of course, our Monte Carlo data are ideal to test approximate analytical theories. We have shown that the hopping model of Burshtein with a cosh-backtransfer correction gives a good semiquantitative description of the steady state fluorescence yield and anisotropy in both two and three dimensions. We believe that the validity of this observation is not restricted to the self-quenching systems that we study here, but also applies to more general systems with a combination of migration and trapping. Therefore, the relative simplicity of heuristic hopping models as compared to more involved theories, such as diagrammatic expansions,[6,7] ATA,[2] CPA,[3] or a diffusion theory,[19] make them very useful. The observed great improvement of the hopping model by inferring the cosh-backtransfer correction, once again proves the very strong nature of this correction, which was pointed out before by numerical calculations[17] and by comparison to an exact density expansion[20] of $N_0(t)$ in pure donor systems. Apparently, random walks in which excitations hop back and forth many times between a donor and its nearest neighbor dominate the transfer kinetics. This idea is confirmed when one generalizes Burshtein's hopping theory systematically, by taking successive groups of p hops (instead of every single hop), to occur in mutually uncorrelated environments. Numerical calculations show that $p = 1$ indeed reproduces the nbt-hopping model, but that convergence to the cosh-hopping model is very slow and not even reached at $p = 10$, the largest value considered.

Finally, we would like to stress that the solid basis for our conclusions lies in the high accuracy of our simulations, as a result of a systematic study and understanding of finite size effects.

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[1] See, for example, the review articles: D. L. Huber, in *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981), Chap. 3; A. I. Burshtein, J. Lumin. **34**, 167 (1985), and references therein.
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[18] Although our definitions for the yield and anisotropy apply to systems without trap absorption and emission, the CRE formalism can of course be extended to include these phenomena. Through the definition of a $M \times M$ relaxation matrix, also containing the (possibly different) intrinsic decay of donors and traps, one derives that then, again, the *total* yield and anisotropy are, as far as the transfer kinetics is concerned, entirely determined by Eqs. (2.7) and (2.8), with exactly the same $D \times D$ matrices.
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